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A Catalyst for Producing Methacrylic Acid and Method for Producing
Methacrylic Acid

[メタクリル酸製造用触媒およびメタクリル酸の製造方法]

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[What is Claimed is:]

[Claim 1]

A catalyst for producing methacrylic acid, which has a chemical composition expressed by formula (1) below, which is used for producing methacrylic acid by gas phase contact oxidation of methacrolein by free oxygen:



(In this formula, P, Mo, V, Cu and O represent phosphorus, molybdenum, vanadium, copper and oxygen respectively. X represents at least one type of element, which is selected from a group of elements made from antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron. Y represents at least one type of element, which is selected from a group of elements made from iron, zinc, chrome, magnesium, tantalum, cobalt, manganese, barium, gallium, cerium and lanthanum. Z represents at least one type of element, which is selected from a group of elements made from potassium, rubidium, cesium and thallium. a, b, c, d, e, f, g and h represent the atomic ratio of each element. When b = 12, a = 0.5 to 3, c = 0.01 to 3, d = 0.01 to 2, e = 0 to 3, f = 0 to 3 and g = 0.01 to 3. h represents the atomic ratio of oxygen, which is necessary to satisfy the atomic

¹ Numbers in the margin display pagination in the foreign text.

valence of each element.), characterized in that said catalyst is manufactured by using a manufacturing method, which includes a process, wherein solution or slurry (solution A) containing at least molybdenum, phosphorus and vanadium is mixed with solution or slurry (solution B) containing an ammonia compound and the resultant mixed solution or slurry (mixed solution AB) is mixed with solution or slurry (solution C) containing element Z, and the amount of ammonium root in solution A is 1.5 mol or less relative to 12 mol of molybdenum atoms in solution A and the amount of ammonium root in mixed solution AB is 6 to 17 mol relative to 12 mol of molybdenum atoms in mixed solution AB.

[Claim 2]

The catalyst as set forth in claim 1 for producing methacrylic acid, characterized in that, before mixed solution AB is mixed with solution C, copper or element Y is mixed with mixed solution AB.

[Claim 3]

A method for manufacturing methacrylic acid, which uses the catalyst as set forth in claim 1 or 2 for producing methacrylic acid.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a catalyst for producing methacrylic acid by gas phase contact oxidation of methacrolein by free oxygen

(hereinafter simply called "catalyst for producing methacrylic acid"), and method for manufacturing methacrylic acid.

[0002]

[Prior Arts]

Among the conventional methods for manufacturing the catalyst for producing methacrylic acid, Japanese unexamined published applications Nos. Hei 4-182450, Hei 5-31368 and Hei 7-185354, Hei 8-157414 and Hei 8-196908 disclose the manufacturing method, wherein two types or more of mixed solution containing elements, which constitute the catalyst, are mixed. Especially, Japanese unexamined published application No. Hei 5-31368 discloses the manufacturing method, wherein solution containing at least molybdenum, phosphorus and vanadium is mixed with solution containing an ammonia compound and the resultant mixed solution is mixed with solution containing cesium element.

[0003]

Also, Japanese unexamined published application No. Hei 9-290162 discloses the method, wherein the pH value of the solution containing all the raw materials for producing the catalyst is adjusted by adding nitric acid or ammonia water to the solution.

[0004]

[Objectives to be Achieved by the Invention]

However, the methacrylic acid yield of the catalyst, which is manufactured by using the above described conventional manufacturing method of mixing raw materials for the catalyst or that of adjusting the pH value of the solution containing said raw materials, is not always sufficient as the industrial catalyst. Currently, its further improvement is sought.

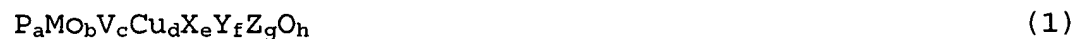
[0005]

Therefore, the present invention attempts to provide a catalyst, which can produce methacrylic acid in good yield by gas phase contact oxidation of methacrolein by free oxygen, and method for manufacturing methacrylic acid.

[0006]

[Means to Achieve the Objectives]

The present invention is a catalyst for producing methacrylic acid, which has a chemical composition expressed by formula (1) below, which is used for producing methacrylic acid by gas phase contact oxidation of methacrolein by free oxygen:



(In this formula, P, Mo, V, Cu and O represent phosphorus, molybdenum, vanadium, copper and oxygen respectively. X represents at least one type of element, which is selected from a group of elements made from

antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron. Y represents at least one type of element, which is selected from a group of elements made from iron, zinc, chrome, magnesium, tantalum, cobalt, manganese, barium, gallium, cerium and lanthanum. Z represents at least one type of element, which is selected from a group of elements made from potassium, rubidium, cesium and thallium. a, b, c, d, e, f, g and h represent the atomic ratio of each element. When $b = 12$, $a = 0.5$ to 3 , $c = 0.01$ to 3 , $d = 0.01$ to 2 , $e = 0$ to 3 , $f = 0$ to 3 and $g = 0.01$ to 3 . h represents the atomic ratio of oxygen, which is necessary to satisfy the atomic valence of each element.), characterized in that said catalyst is manufactured by using a manufacturing method, which includes a process, wherein solution or slurry (solution A) containing at least molybdenum, phosphorus and vanadium is mixed with solution or slurry (solution B) containing an ammonia compound and the resultant mixed solution or slurry (mixed solution AB) is mixed with solution or slurry (solution C) containing element Z, and the amount of ammonium root in solution A is 1.5 mol or less relative to 12 mol of molybdenum atoms in solution A and the amount of ammonium root in mixed solution AB is 6 to 17 mol relative to 12 mol of molybdenum atoms in mixed solution AB.

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[0007]

[Preferred Embodiment of the Invention]

The catalyst of the present invention has the chemical composition expressed by formula (1) above. Manufacturing of the catalyst of the present invention must include the following two processes:

(I) A process, wherein solution A, which is "the solution or slurry containing at least molybdenum, phosphorus and vanadium" is mixed with solution B, which is "the solution or slurry containing an ammonia compound" thereby obtaining mixed solution AB, which is made from solution A and B.

(II) A process, wherein solution C, which is the solution or slurry containing element Z, is mixed with mixed solution AB thereby obtaining solution or slurry containing catalyst precursor.

[0008]

Also, the amount of ammonium root in solution A is 1.5 mol or less, or preferably, 1 mol or less, relative to 12 mol of molybdenum atoms in solution A, and the amount of ammonium root in mixed solution AB is 6 to 17 mol, or preferably, 7 to 15 mol, relative to 12 mol of molybdenum atoms in mixed solution AB.

[0009]

Furthermore, the state of solution A and B and mixed solution AB is not limited to a specific one as long as the raw materials for the catalyst are contained in the solution. It is possible to use solution,

wherein the raw materials for the catalyst are completely dissolved in a solvent, or to use slurry, a part or all of which are suspended in a solvent. Here, as the solvent, it is preferable to use water.

[0010]

The mechanism, wherein the catalyst performance is improved by using the above described manufacturing method, is not unrevealed. However, it is assumed that, by controlling the order of mixing the raw materials for the catalyst and adjusting the amount of ammonium root in solution A and mixed solution AB to a specified amount, it is possible to create the crystalline structure, with which methacrylic acid can be obtained in good yield.

[0012]

Next, the method for manufacturing the catalyst of the present invention will be described more in detail.

(Formulation of solution A)

Solution A is formulated by dissolving or suspending at least molybdenum, phosphorus and vanadium, which are the raw materials for the catalyst, in a solvent, and then, heating and stirring the resultant mixture at 80 to 150 °C, or preferably, 90 to 130 °C for 0.5 to 24 hours, or preferably, 1 to 12 hours. By setting the heating temperature at 80 to 150 °C, it is possible to obtain the catalyst with a high reaction activity to manufacture methacrylic acid. Also, by setting the heating time as 0.5 hour or longer, it is possible

to sufficiently promote the reaction among the raw materials for the catalyst.

[0013]

Solution A is the solution or slurry, which contains at least molybdenum, phosphorus and vanadium, which are the raw materials for the catalyst. In addition to molybdenum, phosphorus and vanadium, solution A may contain elements other than element Z as the raw materials.

[0014]

As the raw materials for the catalyst, which are used for formulating solution A, it is possible to selectively use oxide, nitrate salt, carbonate and ammonium salt of each element. For example, as the raw material for molybdenum, it is preferable to use the one, which does not contain ammonium root, such as molybdic anhydride and molybdenum acid. However, it is possible to use various types of ammonium molybdate such as ammonium paramolybdate, ammonium dimolybdate and ammonium tetramolybdate as long as the amount is small. As the raw material for phosphorus, it is possible to use orthophosphoric acid, phosphorus pentoxide and ammonium phosphate. As the raw material for vanadium, it is possible to use vanadium pentoxide and ammonium metavanadate. Also, as the raw material for molybdenum, phosphorus and vanadium, it is possible to use heteropoly acid such as

phosphomolybdic acid, molybdovanadophosphoric acid and ammonium phosphomolybdate.

[0015]

It is important that the amount of ammonium root in solution A is 1.5 mol or less relative to 12 mol of molybdenum atoms in the solution. Furthermore, to increase the yield of methacrylic acid, it is preferable that the amount of ammonium root in the solution is 1 mol or less. The amount of ammonium root in solution A can be adjusted by changing the amount of the raw materials for the catalyst, which include the ammonium root.

[0016]

(Formulation of solution B)

Solution B is the solution or slurry, which contains an ammonia compound, and is formulated by dissolving or suspending the ammonia compound in a solvent. In addition to the ammonia compound, solution B may contain elements other than element Z as the raw materials as long as said elements do not occupy the entire solution. It is preferable that elements other than the ammonia compound are not contained in the solution. Here, the ammonia compound means the compound or ammonia, which contains ammonium groups. Examples of the ammonia compound include ammonia water, ammonium nitrate, ammonium carbonate and ammonium hydrocarbon.

[0017]

The amount of the ammonia compound in solution B is adjusted so that the amount of ammonium root in mixed solution AB, wherein solution A is mixed with solution B, is 6 to 17 mol, or preferably, 7 to 15 mol, relative to 12 mol of molybdenum atoms in mixed solution AB.

[0018]

(Formulation of solution C)

Solution C is the solution or slurry, which contains element Z, and is formulated by dissolving or suspending element Z as the raw material for the catalyst in a solvent. Solution C may contain elements other than element Z as the raw materials for the catalyst. However, it is preferable that these elements are not contained in solution C. Also, it is preferable that solution C does not contain the ammonia compound. As the raw materials for the catalyst, which are used for formulating solution C, it is possible to selectively use nitrate salt, carbonate and hydroxide. For example, as the raw material for cesium, it is possible to use cesium nitrate, cesium carbonate and cesium hydroxide.

[0019]

(Formulation of mixed solution AB)

According to the present invention, solution A is mixed with solution B thereby obtaining mixed solution AB. The method for mixing solution A with solution B is not limited to a specific one. For example, it

is possible to use a method, wherein solution B is poured into a container containing solution A, or a method, wherein solution A and solution B are simultaneously poured into a container. The obtained mixed solution AB may be heated and aged. To obtain a highly active catalyst, the temperature of solution A and solution B at the time of mixing is preferably 70 °C or lower, or more preferably, 60 °C or lower.

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[0020]

Other raw materials except element Z may be further added to mixed solution AB. The raw materials, which may be added to the mixed solution, can be any materials as long as they are the raw materials for elements except element Z, which are contained in the chemical composition of the catalyst, which is expressed by formula (1) above. The raw materials for the catalyst may be added to mixed solution AB directly or in the state of solution or suspension.

[0021]

(Mixing mixed solution AB with solution C)

According to the present invention, mixed solution AB is mixed with solution C. The method for mixing mixed solution AB with solution C is not limited to a specific one. As the mixing method, it is possible to use a method, wherein solution C is poured into a container containing mixed solution AB, a method, wherein mixed solution AB

is poured into a container containing solution C, or a method, wherein mixed solution AB and solution C are simultaneously poured into a container.

[0022]

According to the present invention, when mixed solution AB is mixed with solution C, it is preferable that mixed solution AB is mixed with copper or element Y and then the resultant mixed solution is mixed with solution C. Here, it is especially preferable that, before copper or element Y, which are the raw materials for the catalyst, is added to mixed solution AB, it is dissolved or suspended in a solvent. As the raw materials for the catalyst, elements other than element Z may be added to mixed solution AB together with copper or element Y. However, it is preferable that these elements are not added at this point. Also, it is preferable that the ammonia compound is not added at this point. As the raw material for the catalyst for copper and element Y, it is possible to selectively use nitrate salt, carbonate and hydroxide. For example, as the raw material for copper, it is possible to use copper nitrate and copper oxide. The method for mixing the mixed solution, which is obtained from mixing mixed solution AB with copper or element Y, with solution C, is not limited to a specific one. The solution or slurry, which is obtained by mixing mixed solution AB with solution C, may be heated and aged. The temperature of both mixed solution AB and solution C at the time of

mixing is not limited to specific one. However, it is preferably 100 °C or lower.

[0023]

(Drying and sintering processes)

After the solution or slurry, which contains all the raw materials for the catalyst, is obtained as described above, the solution or slurry is dried thereby obtaining a dried product of the catalyst precursor. Here, it is possible to use a variety of drying methods. Examples of the drying method include an evaporation drying method, a spray drying method, a drum dryer method and a flash drying method. The type of the dryer, which is used for drying, and the drying temperature are not limited to specific ones. By appropriately changing the drying conditions, it is possible to obtain the desired dried product of the catalyst precursor.

[0024]

Although the dried product of the catalyst precursor may be sintered without being molded, normally, the dried product is molded and then sintered. The molding method is not limited to a specific one. Although various known dry-type and wet-type molding methods can be used, it is preferable that the dried product is molded without having carriers. Examples of the molding method include tablet compression, press molding, extrusion molding and granulation molding. The shape of the molded product is not limited to a specific one. It is possible

to select a desired shape such as a cylindrical column, a ring and spherical shape. Here, when the dried product is molded, a small amount of known additive such as graphite and talc may be added.

[0025]

By sintering the dried product of the catalyst precursor or its molded product, it is possible to obtain the catalyst for producing methacrylic acid. The sintering method and conditions are not limited to specific ones and known sintering methods and conditions can be used. The optimum sintering conditions change depending on the raw materials for the catalyst, composition of the catalyst and method for formulating the catalyst. Normally, the dried product is sintered in circulation of oxygen-containing gas such as air, and/or in circulation of inactive gas, at 200 to 500 °C, or preferably, 300 to 450 °C, for 0.5 hour or longer, or preferably, 1 to 40 hours. Here, the inactive gas means a gaseous body, which does not decrease the reaction activity of the catalyst. Examples of the gaseous body include nitrogen, carbon dioxide gas, helium and argon.

[0026]

When methacrylic acid is produced by using the catalyst, which is manufactured in the manner described above, the raw material gas, which contains methacrolein and free oxygen, is contacted with the catalyst. Although the concentration of methacrolein in the raw material gas can be widely changed, it is 1 to 20 % by volume, or

preferably, 3 to 10 % by volume. Although the raw material gas may contain a small amount of impurities such as water and low grade saturated aldehyde, the amount of the impurities is preferably as small as possible. Although it is economical to use air as the source of the free oxygen, if necessary, it is also possible to use air, which is enriched with pure oxygen. The concentration of the free oxygen in the raw material gas is 0.4 to 4 mol, or preferably, 0.5 to 3 mol, relative to 1 mol of methacrolein. The raw material gas may be diluted with inactive gas such as nitrogen and carbon dioxide gas. Also, moisture vapor may be added to the raw material gas. The reaction pressure of the reaction for producing methacrylic acid is normal to low. Furthermore, although the reaction temperature can be selected from a range of 230 to 450 °C, it is preferably 250 to 400 °C.

[0027]

[Description of the Working Examples]

Next, the present invention will be described more in detail by using working examples and comparative examples. However, the present invention is not limited to the working examples. The "portion(s)" in the working examples and comparative examples means the "portion(s) by weight". The chemical composition of the catalyst was obtained based on the amount of the raw materials for the catalyst elements. The reaction raw materials and the resultant products were analyzed

by using gas chromatography. Here, the reaction rate of methacrolein, selection rate of the obtained methacrylic acid and single current yield of methacrylic acid are defined as follows:

Reaction rate of methacrolein (%) = $(B/A) \times 100$

Selection rate of methacrylic acid (%) = $(C/B) \times 100$

Single current yield of methacrylic acid (%) = $(C/A) \times 100$

Here, A represents the number of moles of methacrolein, which was supplied. B represents the number of moles of methacrolein, which was reacted. C represents the number of moles of methacrylic acid, which was produced.

[0028]

[Working Example 1]

100 portions of molybdic anhydride, 7.34 portions of 85 wt. % phosphoric acid, 4.74 portions of vanadium pentoxide, 0.92 portion of copper oxide and 0.23 portion of iron oxide were added to 400 portions of pure water. The mixture was stirred under reflux for 5 hours thereby obtaining solution A. The amount of ammonium root in solution A was 0 mol relative to 12 mol of molybdenum atoms.

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After solution A was cooled until it was 50 °C, 37.4 portions of 29 wt. % ammonia water, which was solution B, was delivered by drops into solution A and the mixture was stirred for 15 minutes thereby obtaining mixed solution AB. The amount of ammonium root in mixed

solution AB was 11 mol relative to 12 mol of molybdenum atoms. Then, solution, wherein 9.03 portions of cesium nitrate, which was solution C, was dissolved into 30 portions of pure water, was delivered by drops into mixed solution AB. The mixture was stirred for 15 minutes thereby obtaining slurry. The slurry was heated until it was 101 °C. Then, while the slurry was being stirred, it was evaporated to dryness thereby obtaining a solidified product. The obtained solidified product was dried at 130 °C for 16 hours. The resultant dried product was pressure molded and then sintered at 375 °C in circulation of air for 10 hours thereby obtaining a catalyst with the chemical composition of $P_{1.1}Mo_{12}V_{0.9}Cu_{0.2}Fe_{0.05}Cs_{0.8}$. The obtained catalyst was filled into a reaction pipe and mixed gas, which was made of 5 % of methacrolein, 10 % of oxygen, 30 % of moisture vapor and 55 % of nitrogen (percent by volume), 285°C was introduced into the pipe at a contact time of 3.6 seconds. The results are shown in Table 1.

[0029]

[Working Example 2]

Except that 24 portions of 29 wt. % ammonia water was used as solution B so that the amount of ammonium root in mixed solution AB was 6 mol relative to 12 mol of molybdenum atoms, the same conditions were used as those of Working Example 1. The result is shown in Table 1.

[0030]

[Working Example 3]

Except that 51 portions of 29 wt. % ammonia water was used as solution B so that the amount of ammonium root in mixed solution AB was 15 mol relative to 12 mol of molybdenum atoms, the same conditions were used as those of Working Example 1. The result is shown in Table 1.

[0031]

[Working Example 4]

Except that 13.6 portions of 29 wt. % ammonia water was used as solution B so that the amount of ammonium root in mixed solution AB was 4 mol relative to 12 mol of molybdenum atoms, the same conditions were used as those of Working Example 1. The result is shown in Table 1.

[0032]

[Working Example 5]

Except that 68 portions of 29 wt. % ammonia water was used as solution B so that the amount of ammonium root in mixed solution AB was 20 mol relative to 12 mol of molybdenum atoms, the same conditions were used as those of Working Example 1. The result is shown in Table 1.

[0033]

[Working Example 6]

Except that the temperature, at which solution B was delivered by drops, was changed to 80 °C, the same conditions were used as those of Working Example 1. The result is shown in Table 1.

[0034]

[Comparative Example 1]

Except that 13.6 portions of 29 wt. % ammonia water was added to solution A so that the amount of ammonium root in solution A was 4 mol relative to 12 mol of molybdenum atoms and 23.8 portions of 29 wt. % ammonia water was used as solution B so that the amount of ammonium root in mixed solution AB was 11 mol relative to 12 mol of molybdenum atoms, the same conditions were used as those of Working Example 1. The result is shown in Table 1.

[0035]

[Comparative Example 2]

Except that the order of mixing solution B and solution C was reversed and solution C was delivered by drops into solution A and solution B was delivered by drops into the resultant mixture of solution C and solution A, the same conditions were used as those of Working Example 1. The result is shown in Table 1.

[0036]

[Comparative Example 3]

Except that the mixture of solution B and solution C was delivered by drops into solution A, the same conditions were used as those of Working Example 1. The result is shown in Table 1.

[0037]

[Working Example 7]

Solution, wherein 100 portions of molybdic anhydride, 8.88 portions of 85 wt. % phosphoric acid, 4.74 portions of ammonium metavanadate and 1.40 portions of copper nitrate were dissolved in 10 portions of pure water, solution, wherein 2.34 portions of ferric nitrate were dissolved in 10 portions of pure water, 4.11 portions of 60 wt. % arsenic aqueous solution and 1.00 portion of cerium oxide were added to 400 portions of pure water. The mixture was stirred in an autoclave at 120 °C under saturate moisture vapor for 3 hours thereby obtaining solution A. The amount of ammonium root in solution A was 0.7 mol relative to 12 mol of molybdenum atoms. After solution A was cooled until it was 60 °C, solution, wherein 37.0 portions of ammonium carbonate, which was solution B, was dissolved in 80 portions of pure water, was delivered by drops into solution A and the mixture was stirred for 15 minutes thereby obtaining mixed solution AB. The amount of ammonium root in mixed solution AB was 14 mol relative to 12 mol of molybdenum atoms. Then, solution, wherein 18.0 portions of cesium bicarbonate, which was solution C, was dissolved into 30 portions of pure water, was delivered by drops into mixed solution AB. The mixture was stirred for 15 minutes thereby obtaining slurry. The slurry was heated until it was 101 °C. Then, while the slurry was being stirred, it was evaporated to dryness thereby obtaining

a solidified product. The obtained solidified product was dried at 130 °C for 16 hours. The resultant dried product was pressure molded and then sintered at 400 °C in circulation of nitrogen for 5 hours. The obtained sintered product was further sintered at 340 °C in circulation of air for 10 hours thereby obtaining a catalyst with the chemical composition of $P_{1.3}Mo_{12}V_{0.7}Cu_{0.1}Fe_{0.1}As_{0.3}Ce_{0.1}Cs_{1.6}$. Except that the obtained catalyst was used and the reaction temperature was changed to 290 °C, the same conditions were used as those of Working Example 1. The result is shown in Table 1.

[0038]

[Working Example 8]

100 portions of molybdic anhydride, 8.88 portions of 85 wt. % phosphoric acid, 4.74 portions of ammonium metavanadate and 4.11 portions of 60 wt. % arsenic aqueous solution were added to 400 portions of pure water. The mixture was stirred in an autoclave at 120 °C under saturate moisture vapor for 3 hours thereby obtaining solution A. The amount of ammonium root in solution A was 0.7 mol relative to 12 mol of molybdenum atoms. After solution A was cooled until it was 60 °C, solution, wherein 37.0 portions of ammonium carbonate, which was solution B, was dissolved in 80 portions of pure water, was delivered by drops into solution A and the mixture was stirred for 15 minutes thereby obtaining mixed solution AB. The amount of ammonium root in mixed solution AB was 14 mol relative to

12 mol of molybdenum atoms. Then, solution, wherein 1.40 portions of copper nitrate were dissolved in 10 portions of pure water, solution, wherein 2.34 portions of ferric nitrate were dissolved in 10 portions of pure water, and 1.00 portion of cerium oxide were added to mixed solution AB. After that, solution, wherein 18.0 portions of cesium bicarbonate, which was solution C, was dissolved into 30 portions of pure water, was delivered by drops into mixed solution AB. The mixture was stirred for 15 minutes thereby obtaining slurry. The slurry was heated until it was 101 °C. Then, while the slurry was being stirred, it was evaporated to dryness thereby obtaining a solidified product. The obtained solidified product was dried at 130 °C for 16 hours. The resultant dried product was pressure molded and then sintered at 400 °C in circulation of nitrogen for 5 hours. The obtained sintered product was further sintered at 340 °C in circulation of air for 10 hours thereby obtaining a catalyst with the chemical composition of $P_{1.3}Mo_{12}V_{0.7}Cu_{0.1}Fe_{0.1}As_{0.3}Ce_{0.1}Cs_{1.6}$. Except that the obtained catalyst was used and the reaction temperature was changed to 290 °C, the same conditions were used as those of Working Example 1. The result is shown in Table 1.

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[0039]

[Comparative Example 4]

Except that solution A, solution B and solution C were mixed by simultaneously pouring all the solution into a container, the same conditions were used as those of Working Example 7. The result is shown in Table 1.

[0040]

[Table 1]

	Mixing order 1)	Ratio of ammonium root		MAL inversion rate (%) 3)	MAA selection rate 4)	MAA single current yield 5)
		Solution A	Mixed solution AB 2)			
Working Example 1	(A+B)+C		11.0	83.6	82.4	68.9
Working Example 2	(A+B)+C		5.0	83.0	82.8	68.7
Working Example 3	(A+B)+C		15.0	83.3	82.6	68.8
Working Example 4	(A+B)+C		4.0	80.5	83.1	68.9
Working Example 5	(A+B)+C		20.0	79.8	83.4	66.6
Working Example 6	(A+B)+C		11.0	81.5	82.5	67.2
Comparative Example 1	(A+B)+C	4.0	7.0	78.5	83.0	65.2
Comparative Example 2	(A+C)+B		11.0	77.7	83.2	64.6
Comparative Example 3	A+(B+C)		11.0	78.3	83.0	65.0
Working Example 7	(A+B)+C	0.7	13.3	80.3	83.5	67.1
Working Example 8	(A+B)+C	0.7	13.3	81.2	83.6	67.9
Comparative Example 4	(A+B)+C	0.7	13.3	76.5	83.4	63.8

1) Each code in the column "Mixing order" means as follows:

(A+B)+C: After solution B was added to solution A, solution C was added.

(A+C)+B: After solution C was added to solution A, solution B was added.

A+(B+C): Solution, wherein solution B was mixed with solution C, was added to solution A.

(A+B+C): Solution A, solution B and solution C were simultaneously mixed.

2) When the mixing order is other than (A+B)+C, the ratio of ammonium root in mixed solution AB means the ratio of ammonium root in the mixed solution containing solution C.

3) MAL represents methacrolein.

4) MAA represents methacrylic acid.

[0041]

[Effect of the Invention]

By using the catalyst of the present invention, it is possible to produce methacrylic acid in good yield.